

CERAMICS AND INTERMETALLICS

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CERAMICS AND INTERMETALLICS

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Introduction

This report covers the state of the art, applications, and future requirements of the refractory ceramics and intermetallic compounds of most interest to the Air Force for structural and non-structural considerations. Materials for electronic and electrical uses are not included.

An Ad Hoc committee of the Materials Advisory Board, National Academy of Sciences, and National Research Council recently completed a thorough study of the state of the art of refractory inorganic nonmetallic structural materials on request of the Office of the Director of Defense Research and Engineering. Because of the thoroughness of the study and excellence of the report, Report MAB-169-M, permission was requested and received from the Office of the Director of Defense Research and Engineering to use selected major portions of the MAB Ad Hoc Committee report. The following sections of the MAB report were used practically intact: Borides, Beryllides (the only intermetallic compounds the Ad Hoc Committee felt were of interest as structural materials), Carbides, Nitrides, Silicides, Oxides, and Brittle Behavior (the section which treats certain problems as microstructure, fracture and flow phenomena, etc., which were common to all the material classes).

The Ad Hoc Committee was composed of the following individuals: Dr Wingate A. Lambertson - Chairman (The Carborundum Company), Dr Neil N. Ault (Norton Company), Mr John C. Bowman (National Carbon Research Laboratory), Mr Samuel W. Bradstreet (Armour Research Foundation), Mr Winston H. Duckworth (Battelle Memorial Institute), Dr Einar P. Flint (Arthur D. Little, Inc.), Dr William W. Shaver (Corning Glass Works), Dr Hans Thurnauer (Minnesota Mining and Manufacturing Co.). The consultants to the Committee were: Dr R. T. Dolloff of the National Carbon Research Laboratory (Carbides), Mr Wilfred H. Dukes of the Bell Aerosystems Company (Structures and Design). The Materials Advisory Board Staff Consultant was Mr Jerome J. Krochmal (on loan from the Air Force).

Borides

The borides are a highly refractory group of ceramic materials characterized by extreme hardness and high electrical conductivity to high temperatures. They have not been studied extensively and, as a result, data on composition and melting points are often incomplete. There appear to be more than 30 binary borides with melting points greater than 2000°C (3632°F). Those of most interest as structural materials are zirconium boride (ZrB_2), titanium boride (TiB_2), niobium boride (NbB_2), tantalum boride (TaB_2), hafnium boride (HfB_2), and thorium boride (ThB_2). Exhibiting more promise than the binaries are the mixed borides of at least ternary systems.

Titanium diboride and zirconium diboride powders and simple fabricated shapes are available in commercial quantity from several suppliers at about \$10/lb, but the other

borides are essentially experimental materials. The application of these borides has been limited since there has been no demand for these materials in commercial quantities.

The techniques ordinarily used for fabrication of parts from these borides are either molding and sintering, or hot pressing. Coatings of the borides have been prepared by flame-spraying with arc plasma equipment. High density products of these materials can now be made by hot molding which is a commercial process suitable for making simple shapes up to 1-1/2 feet in diameter and approximately the same height. Literature data on strength properties of these materials were obtained on products fabricated by hot pressing. The purity of such products is usually greater than 97 per cent, but very little work has been done with really high purity material.

Ten years ago some government-sponsored research was done on metal-bonded borides for use as turbine blades. This work showed that the metal-bonded borides did not have sufficient impact resistance for this application. The metal bond used in these studies limited their use to about the softening temperature of the alloy. Within the last two years, data generated from several sources indicates promising properties for the borides. Considerable work is being done in industry on the use of titanium or zirconium boride as cathode bars for aluminum reduction cells. These materials have also been used for aluminum vaporizing boats.

One disadvantage of the borides is that, like most inorganic nonmetallic materials, they do not have toughness at room temperature. They are probably not ductile at any useful temperature. The high strength and the hardness of the borides are desirable properties of the materials but also disadvantageous in another respect because they make them hard to fabricate. Fabricated pieces cannot be machined; finishing operations require diamond grinding.

Properties

It should be repeated that the data on borides are limited and ultimate potentials have not been fully determined.

Chemical Stability

Borides are stable compounds to very high temperatures, and are inert to the oxides. Titanium and zirconium borides are known to be stable in the presence of tungsten, molybdenum, and graphite. Thus the borides should be excellent materials to use in composite structures because they are compatible with and can be used in contact with other structural materials to extremely high temperatures.

Of the simple borides, zirconium and titanium diborides have the best oxidation resistance, being resistant to 1300°C (2372°F) and 1400°C (2552°F), respectively, for extended periods of time. Boron, which oxidizes to a glass-forming oxide, promotes oxidation resistance of the borides and there is good evidence that even better oxidation resistance can be obtained by additions to the boride compositions. It is also likely that higher temperature-stable oxide coatings can be produced on the borides more readily than on metals or carbides.

A dramatic example of an improvement in oxidation resistance is obtained from a body made of 90-percent zirconium boride and 10 percent molybdenum disilicide. The rate of oxidation of this material after one hour at 1950°C (3542°F) is 40-45 mg/cm²/hour. After one hour under these conditions an oxide layer 0.6 mm thick is formed. The oxidation rate

for a four-hour oxidation test at 1950°C (3542°F) is 16 mg/cm²/hour and the oxide layer is about 1 mm thick. At lower temperatures, the oxidation rates are considerably reduced.*

Mechanical Properties

The flexural strength of titanium diboride at 96 percent of theoretical density has been observed at 35,000 psi from 25°C (77°F) to 2000°C (3632°F). The modulus of elasticity of this product was 60×10^6 psi, and the hardness 3300 kg/mm² Vickers** (comparable to Knoop). The compressive strength of titanium diboride from another source has been measured at 97,000 psi. For zirconium boride, modulus of rupture values are reported from 8,000-29,000 psi. These are inconsistent with tensile strength values in the literature of 28,700 psi. The modulus of elasticity is reported as 50×10^6 psi.

Some data are available on the mechanical properties of the 90 percent zirconium boride, 10 percent molybdenum disilicide body discussed above. This composition has a modulus of rupture of 38,800 psi at room temperature which decreases to 13,000 psi at 1500°C (2732°F). The modulus of elasticity of this product at a density of 5.74 g/cc is 46×10^6 psi.

Thermal Properties

Thermal conductivity data near room temperature show values of 0.03 to 0.06 cal cm sec⁻¹ C⁻¹ with a positive temperature coefficient for the borides of titanium, zirconium, tantalum, and niobium.

The electrical resistivity of the borides also has a positive temperature coefficient and the borides are good electrical conductors. The resistivities of zirconium and titanium diborides are approximately 10-20 micro-ohm centimeters at room temperature.

The thermal expansion coefficient for zirconium boride is $7.3 \times 10^{-6}/C$ from room temperature to 1000°C (1832°F) and for titanium boride is $8.1 \times 10^{-6}/C$ to 1000°C (1832°F).*** Table 1 gives literature data on melting points.

Recently initiated efforts sponsored by the Department of Defense are expected to provide the thermochemical kinetic information which is required for theoretical evaluations on the use of the borides of hafnium and zirconium under conditions of vacuum, atmospheres of O₂, O₂ + H₂O, F₂, HF, Cl₂, N, NH₃, CO, or H₂, and temperatures to 2750°C (4982°F).

Thermal Shock

Considering the thermal and mechanical characteristics, the borides are expected to have relatively good thermal shock resistance when compared with other ceramic materials.

It is interesting that a thermal cycling test on the 90 percent ZrB₂, 10 percent MoSi₂ body showed a 50 percent increase in strength after 30 cycles from room temperature to 1350°C (2462°F) with cooling in an air blast, whereas an alumina specimen failed after two cycles.

* Unpublished Carborundum Company data.

** Unpublished National Carbon Company data.

*** Unpublished Norton Company data.

Potential Properties

The property data on the borides is very meager, and their potential is just becoming evident. On the basis of recent determinations on titanium boride, the strength-weight ratio is not exceeded by any other bulk material from 1600°C (2912°F) to above 2000°C (3632°F) and this high strength is probably maintained to at least 2200°C (3992°F). The borides are just beginning to be studied in detail, and the data to date is for borides of 98-99 percent purity.

The borides appear to be the only materials which can be used under the oxidizing conditions, supporting substantial loads for an extended period of time from 1600°C (2912°F) to 2200°C (3992°F). They will probably be used below and above these temperatures as well, but below 1600°C (2912°F), they must compete with refractory metals and intermetallics, and above 2200°C (3992°F), with graphite and the carbides.

Boride References

1. Brewer, Sawyer, et al, "A Study of Refractory Borides," J. Amer. Cer. Soc., Vol 34, No. 6, pp 173-179, (1951).
2. Campbell, I. E., "High Temperature Technology," John Wiley and Sons, Inc., New York, (1956).
3. Smiley, Sobon, et al (Standard Research Institute), "Mechanical Property Survey of Refractory Nonmetallic Crystalline Materials and Intermetallic Compounds," WADC Technical Report 59-448, January 1960.

Beryllides

The beryllides, having first been considered during the middle 1940's under the NEPA Program, constitute a fairly new addition to the many classes of refractory materials. Activities were curtailed until about 1956 when a comprehensive literature survey of approximately 800 binary systems was accomplished, resulting in the selection of about 70 compounds with melting points of higher than 1400°C (2552°F) having potential for satisfying a combination of structural and nuclear requirements. A number of these compounds which included aluminides, silicides, beryllides, zirconides, germanides, chromides, and ferrides, were screened experimentally and several silicides, aluminides, and beryllides passed initial oxidation screening tests in the temperature range of 1260°C (2300°F) to 1370°C (2498°F) by exhibiting less than 2 mils penetration after 100 hours of exposure. Continued and accelerated activity was directed toward structural as well as nuclear application potential. Minimum temperature levels prerequisites were considered also, resulting in finally limiting activity to the beryllides and silicides. Silicides, except for comparison, will not be discussed here, since they are considered as another class of materials warranting individual attention.

State of the Art

The most promising beryllides appear to be those of zirconium, hafnium, niobium, molybdenum, and tantalum. Available data indicate that the more oxidation resistant compounds are the higher beryllides such as M_9Be_{17} , MBe_{18} , and MBe_{19} . Mixtures of beryllides in a given reactive metal system will normally exhibit, in addition to excellent

oxidation resistance, considerably higher strengths than can be attained with any compound in that system (see figure 1). Excellent crystallographic work has been evidenced by the identification of these complex species.

Efforts to date have employed mainly impure starting materials, primarily Be, with major impurities being BeO (1.5%), Be₂C (.15%), and Fe (.08%). These impurities appear in the microstructure, both at the grain boundaries and as individual grains. Some attention has been given to microstructure, although most variations in grain size have been in the range of 10 to 25 microns. Recent activity has been directed toward achieving higher purities, but little or no accompanying property data is yet available. The purer beryllium powders are still rather dirty in comparison to what one thinks of in terms of high purity metal powders.

Melting point determinations have been accomplished and are generally cited as accurate to within $\pm 50^{\circ}\text{C}$ (90°F). Considering the melting point data from different facilities, there is generally agreement to within $\pm 75^{\circ}\text{C}$ (135°F), the principal difficulty is compositional changes due to the high vapor pressure of beryllium.

Continued investigations of mechanical properties (primarily modulus of rupture), oxidation resistance, and Young's Modulus, indicate that maximum utilization temperatures for the compounds of interest fall within the range of 1150°C to 1620°C (2102°F to 2948°F).

Thermal expansion coefficients, thermal conductivities, and heat capacities have been and are being determined. Oxidation studies have given primary consideration to the use of "laboratory" air but efforts are underway to elucidate the effects of wet air upon the BeO scale formed during the oxidation process. The kinetics and mechanisms of the oxidation processes are being studied or will be studied in the near future.

The process employed in the fabrication of shapes is hot-pressing with maximum pressures of approximately 2,000 psi at temperatures of 1540°C to 1650°C (2804°F to 3002°F), resulting in compacts ranging from 97 to close to 100 percent of the absolute density. Other ceramic fabrication processes, as well as mechanical working are being investigated.

Current Applications

Beryllides are currently not in use but offer excellent potential for early utilization in nuclear applications and other applications requiring high strength-to-weight ratio materials that have inherent oxidation resistance as well as thermal shock resistance to temperatures of 1620°C (2948°F). Potential applications would include leading edges, wing and body panels, nose cone skirts, bearings, supporting structures in hot areas of propulsion systems, etc. Utilization in space applications such as radiators, sinks, hot structures, etc., probably cannot be considered at temperatures in excess of 1540°C (2804°F) due to the expected deleterious effects of "hard" vacuum.

Advantages and Disadvantages

High strength, light weight, good oxidation resistance, and good thermal shock resistance, place the beryllides in a favorable position for satisfying potential requirements for materials in the temperature range to 1650°C (3002°F). Since advantages and disadvantages are meaningful in only a relative sense, a discussion must include those materials which are seemingly competitive on an "across-the-board" basis, viz, the silicides including that of carbon (SiC) and the refractory metals when suitably protected.

The beryllides have a very favorable degree of oxidation resistance when compared with the silicides, each of which (MoSi_2 , TaSi_2 , and WSi_2) exhibits the formation of a "pest." While a high temperature preoxidation treatment will preclude the formation of these "pests", such treatment is analogous to the protection afforded by a coating which is amenable to damage.

With regard to strength, it would appear that insufficient data are available to truly compare the beryllides with the silicides. Table 2, however, does indicate, even though on the basis of a very meager number of data points, that the beryllides are competitive with the silicides on a strength-density basis. Comparing the beryllides with silicon carbide, it is noted that relative strengths plus the ability of the beryllides to yield locally in regions of stress concentrations, would favor the beryllides over the most advanced form of silicon carbide available today (i.e., KT silicon carbide). The beryllides also offer, as a future possibility, some room temperature ductility which, in all probability cannot be expected from silicon carbide, a covalently-bonded material.

Competition from the refractory metals would be primarily from suitably protected molybdenum (or its alloys) which, although perhaps brittle at lower temperatures, is nevertheless quite ductile when compared with the beryllides. One hundred hour oxidation tests at temperatures from 1480°C to 1600°C (2696°F to 2912°F) are beyond the capability of even the best molybdenum coatings available to date, and years of activity devoted to this problem seemingly indicate that future progress will be meager or perhaps nil. In contrast, the beryllide picture is one of optimism, and justly so, for the elimination of a substantial percentage of impurities contained at present, and the benefits that are logically to be expected from microstructural improvements, will tend to improve low-temperature ductility.

The cost of beryllium powder is at present approximately \$79 a pound and would in all probability be substantially higher if it were obtainable in higher purity than that cited previously. If beryllium comes into widespread use as a metal, the supply factor could conceivably reach critical proportions; however, the potential beryllide utilization will probably constitute such a small fraction of industrial beryllium capacity that the supply variable is really of little significance. It is also noted that new ore deposits have been and are being discovered, and although assays are low by present standards, it is not unreasonable to expect technological improvements to permit efficient extraction.

No discussion of the pros and cons of anything containing beryllium is complete without a few words relative to the strict dust control procedures necessary to avoid toxicity hazards. It has been shown in a number of current beryllia facilities that sound industrial hygiene practices are really all that are required to cope with this problem.

Properties

Chemical Stability

The higher beryllides have varying degrees of oxidation resistance to 1600°C (2912°F) as illustrated in figure 2. Table 3 presents some short-time, high temperature, oxidation resistance data for the beryllides and silicides. The superiority of the silicides at 1650°C (3002°F) is evident. The oxidation-resistant characteristics of the beryllides are attributable to the formation of a tenacious BeO film separated from the original beryllide composition by a beryllium-depleted film. Oxidation characteristics at 1650°C (3002°F) may be described more accurately as degradation due to the high vapor-pressure of beryllium.

Physical and Mechanical Properties

Table 2 cites some typical physical and mechanical properties of both selected beryllides and silicides. Figure 1 indicates mechanical property trends and it should be noted that there is a paucity of data for temperatures below 1260°C (2300°F).

Thermal Shock

Thermal shock resistance is reported to be good when specimens are cycled between room temperature and 1260°C to 1620°C (2300°F to 2948°F). Some poor thermal shock resistance has been noted when specimens have been cycled between room temperature and 870°C (1598°F) and it is noted that this temperature coincides with the lowest exhibited modulus of rupture values.

Potential Properties

Considering the attached modulus of rupture versus temperature plots and recognizing that densities are not theoretical, grain sizes are fairly large, and in addition, that impurities are scattered throughout the structure in the form of massive agglomerates, it is reasonable to expect at least a twofold improvement in mechanical properties with some success in the correction of such deficiencies. Improvements that may be expected from ultra-high purity, which will eliminate grain-boundary impurities and the dispersed agglomerates are:

- a. Improved low-temperature strength (presently contained agglomerates constitute stress raisers)
- b. Improved high-temperature strength (creep at high temperatures may be attributed to grain boundary impurities)
- c. Improved ductility at low temperatures
- d. Improved ductility at higher temperatures

Mechanical working offers additional possibilities to improve strengths. Modulus of rupture values of 50,000 to 70,000 psi at room temperature for the lower density beryllides or from 90,000 to 125,000 psi for the heavier beryllides, will result in strength-density ratios of from 500,000 to 700,000 inches while at 1510°C (2750°F), modulus of rupture values of 40,000 and 72,000 psi for the lighter and heavier beryllides, respectively, will result in a strength-density ratio of 400,000 inches. These values are considered within reach of the better beryllides.

Oxidation resistance will be improved to a minor degree with the $\frac{1}{2}$ to $1\frac{1}{2}$ percent increase in density to the 100 percent value.

Alloy compositions are anticipated which will provide improved low-temperature ductility and the resultant compromise of high-temperature strengths, though significant from an overall standpoint, may still provide 10,000 psi modulus of rupture at 1510°C (2750°F).

The beryllides also offer promise for use both as coatings and diffusion barriers for refractory metal protection.

Beryllides References

1. Paine, Stonehouse and Beaver, "An Investigation of Intermetallic Compounds for Very High Temperature Applications," Brush Beryllium Company, WADC TR 59-29, Part I (January 1960); Part II (July 1960).
2. Booker, Paine, and Stonehouse, "Investigation of Intermetallic Compounds for Very High Temperature Applications," Progress Reports Nos. 1 (15 Aug 1959); 2 (15 Nov 1959); 3 (15 Feb 1960); 4 (15 April 1960); 5 (15 July 1960).
3. Beryllide Conference, Cleveland, Ohio; 1, 2 June 1960; Proceedings to be published.

Carbides

The highest melting temperatures known today are found among the carbides. Interest in the carbides of the transition metals, Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, W, and in the carbides of B, Be, Si, U and Th, stems mainly from the high melting temperatures, which indicate potentially high service temperatures, and from the high values of measured hardness, which predict very high ultimate strengths. Achieving hardware of high service temperature and high strength in these materials has not been satisfactorily met at present because of the great difficulties encountered in the chemical synthesis of characteristic, clean materials and in the reproducible fabrication of these materials into useful shapes. The magnitude of the difficulties is directly related to the high melting points — the characteristic which created the high interest.

State of the Art

Almost without exception the carbides of today are formed by powder methods. The same high melting points that predict ultimately high service temperatures make it necessary to use high temperatures in forming the basic materials and in fabricating them into useful shapes. Today's carbides are usually the result of arbitrary mixtures of particles, generally of unknown size distribution, and of a chemical nature only 98 percent defined. These are sintered or hot-pressed under a protective atmosphere which may contain an unknown amount of oxygen, nitrogen, or other active gases. The unknown 2 percent of the article may consist of any number of impurities or unidentified phases. Usually little is known about the surface layers on the particles either before, during, or after processing, because of the difficulties associated with identification. The measured properties, on the other hand, depend as much on these intergranular phases as on the basic material. The problem is thus similar to that of the ceramic oxides, but it is complicated by the fact that surface oxides in carbide bodies represent foreign, and usually detrimental, phases.

Techniques for the formation of carbide shapes have improved somewhat in the past decade to the point where reasonably high densities can be obtained in simple geometrical shapes. Such processes, however, usually require the use of high pressures at high temperatures. More complicated shapes can be obtained by precompaction, followed by sintering, but here final density is sacrificed with resultant general deterioration in mechanical strength and corrosion resistance.

Current Applications

Cobalt-bonded tungsten carbide is widely used as a cutting tool material because of its toughness at moderately high temperatures. This material is specialized, however, in that many of its useful properties stem from the binder used and, as a consequence, it is limited by the binder. Similar binders have not been found for other carbides and specific properties required for the binder phase are not recognized clearly.

The self-bonded carbides do not enjoy widespread use because they are difficult to fabricate, the cost is relatively high, and they are brittle. Many applications to date have been restricted to coatings where the abrasion resistance, hardness, and generally good chemical resistance are useful. Applications outside the coating area include crucibles for laboratory use where special chemical properties at high temperatures are required. In addition, the materials are employed where simple geometrical shapes are suitable. Examples of these include controlled resistivity SiC for heating elements, low density SiC for kiln furniture, and UC₂ rods for nuclear fuel elements. The fuel rod application usually requires a clad material for the purpose of retaining the fission products.

Advantages, Disadvantages, and Limitations

The melting temperatures of the carbides are higher than those of any other class of materials. Carbides must, therefore, be considered for use at temperatures where most materials are no longer solid and structural elements are needed.

Favorable characteristics of carbides include excellent chemical stability toward other materials, high hardness, good abrasion resistance, and reasonable strength at moderately high temperatures. A limiting characteristic is oxidation resistance. With the exception of SiC, which has a use temperature of 1600°C (2912°F) under oxidation conditions; none of the carbides can be used at temperatures exceeding 1000°C (1832°F) for long-time periods when oxygen is present.

Lack of ductility is also a limiting carbide property. While there is hope that brittleness can be reduced by close control of impurity phases and by close attention to particle shape, size, and distribution, there is no scientific evidence that this class of materials can be made nonbrittle. To date there has been no systematic approach to the problem by means of fundamental investigations of the mechanical properties of well-characterized, high purity samples. The similarity of the crystal structure of the transition metal monocarbides to that of the ductile metals, taken together with the existence of at least partial metallic bonding in these carbides, lends hope to the thesis that these materials may be inherently nonbrittle. On the other hand, the observed relations between brittle fracture and perfection of surfaces make it clear that the translation from nonbrittle laboratory specimens to full-scale, nonbrittle hardware may never be successfully accomplished.

Other difficulties with the carbides include the hardness and abrasion resistance. These properties (assets in the finished articles) act as handicaps in the fabrication processes. Shaping must be accomplished prior to final synthesis because machining is difficult. Thus, geometrical tolerances are obtained only at greatly increased expense.

Properties

The following paragraphs present a brief summary of the chemical and physical properties of the refractory carbides. Ranges of properties, rather than specific tabulations,

are given because many of the data are incomplete and because many of the reported values are strongly dependent on specific sample preparation methods.

Chemical Stability

The transition metal carbides of the fourth, fifth, and sixth columns and the carbides of B, Be, Si, Th, and U, are stable compounds having relatively large negative heats of formation. In comparison with oxides, borides, and nitrides, the carbides fall below the more stable oxides, above the nitrides, and are roughly equivalent to the borides.

The oxidation resistance of the carbides is not outstanding; the majority oxidize readily at temperatures approaching 1000°C (1832°F). Protective coatings are necessary for continued use at this temperature. SiC is an exception to this rule in that the oxidation product serves as a protective coating which permits use temperatures as high as 1600°C (2912°F) for extended time periods.

The carbides are chemically inert at ordinary temperatures. They resist reducing atmospheres and they volatilize only very slowly under vacuum conditions at temperatures approaching their melting points.

The carbides are fairly stable toward nitrogen. TiC for instance, has been reported in nitrogen at 2500°C (4532°F). One of the highest melting carbides, TaC, is unaffected by nitrogen to 3000°C (5432°F) provided there is no hydrogen present.

Strength and Modulus of Elasticity

Room temperature mechanical data on the carbides show a considerable variation from specimen-to-specimen. Reported moduli of elasticity vary between 30×10^6 psi for Mo₂C to 100×10^6 psi for WC with variations of as much as 75 percent of the mean for any particular carbide. Tensile strengths range from 5,000 to 80,000 psi; compressive strengths vary from 80,000 to 600,000 psi and flexural strengths cover the interval from 10,000 to 120,000 psi with variations as high as 85 percent of the mean for given carbides.

Strength measurements at temperatures above 1500°C (2732°F) have been made for only a limited number of carbides. SiC flexural strength is practically unaffected up to temperatures of 1500°C (2732°F) with values as high as 70,000 psi reported. Cr₃C₂ shows an increase in flexural strengths, with increasing temperature, from about 43,000 to 80,000 psi at 1100°C (2012°F), followed by a sharp decrease at higher temperatures. B₄C, ZrC, and TiC all exhibit decreased flexural strength with temperature increase to 1200°C (2192°F) or higher. In only a few cases have measurements been carried out at temperatures up to 2000°C (3632°F) with strength values reported in the range of 20,000 psi in flexure for mixed carbides.

High-temperature moduli of elasticity have been reported for SiC and Be₂C. For Be₂C the modulus drops from 26 to 12×10^6 psi as the temperature is increased to 1100°C (2012°F). For SiC the modulus decreases slightly or increases, depending on the sample, to a 1550°C (2822°F) value of about 40×10^6 psi. No high-temperature modulus of elasticity data have been reported for the other carbides.

It is apparent that data on high-temperature strengths and moduli of elasticity are scarce in the range up to 1500°C (2732°F) and practically nonexistent at higher temperatures. More of this data is needed for a valid evaluation of carbide potentials. The influ-

ence of grain size, growth and orientation, as well as density and type of porosity, must also be evaluated further.

Thermal Properties

The highest reported melting point, 3940°C (7124°F), is for the complex carbide, 4TaC:HfC. Six of the simple carbides, TiC, ZrC, HfC, NbC, Ta₆C, and TaC melt at temperatures in excess of 3000°C (5432°F) and most of the others under discussion melt above 2000°C (3632°F).

Coefficients of thermal expansion range from a low of $4.5 \times 10^{-6}/\text{C}$ for B₄C and SiC to a high of $12.5 \times 10^{-6}/\text{C}$ for UC₂; thermal conductivities are as low as 0.034 cal/cm sec C for CbC and as high as 0.1 cal/cm sec C for SiC; specific heats have a low of 0.04 cal/g C for WC and a high of 0.16 cal/g C for SiC; thermal emissivities, for which data is very incomplete, range from 0.2 to 0.4.

The majority of this thermal data is subject to the same criticisms as the mechanical data. They depend strongly on the nature of the sample, its chemical composition, purity, grain size and distribution, density, and porosity. With the exception of the very high melting points, and the somewhat unique characteristics of SiC, the thermal properties of carbides are not extraordinary.

Thermal Shock

With the exception of SiC, whose service range has an upper limit of about 1600°C (2912°F), none of the carbides can be classified as having good thermal shock resistance. To date, very little work has been done to determine how the factors — such as grain size and orientation, porosity type and distribution, additives phases — can be varied to improve strength and thus thermal shock properties. The first significant program to determine factors of this type in a typical carbide such as ZrC has only recently begun. The results to date are encouraging. It is not apparent, however, that orders-of-magnitude improvement will be achieved in the thermal shock parameter by manipulation of the parameters involved without possible adverse effects on other important properties such as high-temperature strength.

Potential Properties

It is difficult to predict the ultimate properties attainable in the carbides because pertinent information is not available. While many properties have been measured and reported, in almost no case has relevant data been reported on sample purity, stoichiometry, grain size, distribution and orientation, porosity or particle surface chemistry. Since the observed properties are strongly dependent on these factors and since these data are usually not known, extrapolation of the observed properties in terms of future potential cannot be accomplished with a high degree of certainty.

Temperature data in the range from 1000°C (1832°F) to 2500°C (4532°F) is particularly conspicuous by its almost complete absence. Data is needed on strengths, elastic moduli, thermal conductivities, and coefficients of expansion — all determined as functions of temperature and correlated with the sample purity, grain size, porosity, and other controlling microproperties to determine the potential usefulness of the carbides.

A single series of experiments indicates that useful high-temperature strengths can be obtained in the carbides. This observation is based on evidence that the addition of a low

elastic modulus material, such as graphite, to a carbide, such as ZrC, may improve the thermal shock parameter of the body while improving the high-temperature strength. In the cited instances, the addition of 20 percent resulted in a modulus of rupture of 9,000 psi at 1750°C (3182°F), a value twice that of the ZrC alone. The strength of the composite exceeded that of the base material throughout the entire range above room temperature.

Experiments of this nature indicate that significant progress may be expected through specific research applied to the problem of optimizing high-temperature properties in carbides. There is little doubt that careful and imaginative studies in this and related areas, on well-characterized carbide materials, will lead to structural materials with useful strengths at temperatures approaching 2500°C (4532°F).

Carbide References

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2. Campbell, I. E., "High Temperature Technology," John Wiley and Sons, (1956).
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5. WADC Technical Report 59-448, "Mechanical Property Survey of Refractory Non-metallic Crystalline Materials and Intermetallic Compounds," January 1960.
6. "Proceedings of an International Symposium on High Temperature Technology," McGraw-Hill Book Company, 1960.
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Nitrides

There are several nitrides known to have interestingly high melting points. Of these, the interstitial nitrides of Sc, Ti, Zr, Hf, V, Nb, Ta, Th, and U appear to be sufficiently resistant to dissociation, to consider them as refractory. Dissociation pressures of the interstitial nitrides, of Cr, Mo, and W are considered to be too high for them to be interesting. Of the covalent nitrides, Be, B, Al, and Si are refractory. Several other nitrides, particularly the interstitial nitrides of La, Ce, Pr, and Nd, are suspected of being refractory enough to consider here, but data on their melting and dissociation temperatures is lacking.

State of the Art

Of the refractory nitrides, commercial products are made only of BN, AlN, and Si₃N₄, and the production of these is limited. Probably the commercial status can be summed up, more or less, for each as "potential applications are being explored"

There has been little Government research on refractory-nitride ceramics. TiN and ZrN were investigated as crucible materials and, cursorily, for rocket nozzles several years ago, and the AEC has looked at UN ceramic for use as nuclear fuels.

Advantages and Limitations

The nitrides are not notably oxidation resistant. This deficiency and, except for the case of BN, no clearly unique qualities account for the inactivity on nitride ceramics. With the exception of Si_3N_4 , none could be recommended unequivocally for use in air above 1100°C (2012°F). The nitrides of Be, Al, Sc, La, Ce, Pr, Nd, Th, and U also are reported to react with water vapor.

Because it has crystal structures similar to graphite and diamond, with slightly better oxidation resistance than the other nitrides, BN is probably the most interesting for structural use. Efforts to self-sinter hexagonal BN powder have been unsuccessful, and like graphite, bodies made from it to date contain a binder. Data are available on a body* containing 2.4 percent B_2O_3 made by hot pressing. It has several similarities to graphite:

1. Directionality in properties.
2. Easily machineable, but not quite so soft as graphite.
3. High thermal conductivity ($100\text{-}200 \text{ Btu/ft}^2/\text{in/hr}/^\circ\text{F}$).
4. Excellent resistance to thermal shock.
5. Slight resiliency.
6. Low density (body density - 2.1 g/cm^3 ; crystal density - 2.25 g/cm^3).

Its room-temperature strength (15,900 and 7,300 psi modulus of rupture, depending on direction) is somewhat higher than that of graphite. But, in the range from about 982°C (1800°F) to 1482°C (2700°F), the strength drops to 1000 - 2000 psi. At higher temperatures the strength increases, approaching the room temperature value at 2400°C (4352°F). This rather odd strength-temperature behavior, characteristic of oxide-bonded BN, is closely associated with the binder.

Unlike graphite BN is an electrical insulator which, depending on the application, could be advantageous. The resistivity of the above body is reported to be:

<u>TEMPERATURE, C</u>	<u>RESISTIVITY, ohm - cm</u>
25 (77°F)	10^{13}
500 (932°F)	10^{10}
1000 (1832°F)	10^5

In another experiment a resistivity of 10^{14} ohm-cm at 500°C has been reported.

BN is reported to have excellent oxidation resistance to 700°C (1292°F), and not to be wetted by many molten metals and salts. A disadvantage is its tendency to hydrolyze; its performance as a rocket nozzle, for example, is improved by thorough drying before testing.

* Carborundum Company

Cubic BN has been made by methods used to produce synthetic diamond, and has a hardness in the range of diamond.

Concerning the other refractory nitrides, moduli of rupture of 11,500 and 20,000 psi were reported for ceramics of AlN and Si₃N₄, respectively, at room temperature. Another AlN ceramic prepared by hot pressing was reported to have a modulus of rupture of 38,500 psi at room temperature and 18,000 psi at 1400°C (2552°F); its modulus of elasticity at room temperature was 50 × 10⁶ psi. A ceramic of Si₃N₄ was reported to lose "little" strength with temperature increases to 1100°C (2012°F). Thermal shock resistance of AlN or Si₃N₄ is reported to be "good".

Silicides

State of the Art

Methods that have been or can be used in preparing the silicides in powder form are the following: (1) synthesis by fusion or sintering (2) reduction of metal oxides with silicon (3) reaction of metal oxides with SiO₂ and C (4) reduction of mixtures of silica and metal oxides by means of a thermite reaction (5) reaction in a molten alloy (6) reaction of metal with silicon halide or metal halide with silicon, or simultaneous decomposition of metal and silicon halides, and (7) fused salt electrolysis.

Pure silicides can be formed by sintering together a finely-divided mixture of silicon and the appropriate metal, if sintering is sufficiently prolonged and if there is intermediate grinding and remixing between several sintering steps to assure homogeneity. The simultaneous thermal decomposition of a mixture of a volatile metal chloride with one or more of the silanes should be capable of producing pure metal silicides.

Once the silicides have been prepared in pure form, it is necessary to exercise care in subsequent processing. With molybdenum disilicide, for example, it is necessary to crush and grind the material in a neutral atmosphere or under an unreactive liquid. Otherwise, even with the moderate amount of heat developed during these operations, oxidation of the surface of the disilicide particles will occur.

Current Applications

Only a narrow range of applications has been found for any of the silicides. Molybdenum disilicide has received much study as a coating for molybdenum and other materials that are susceptible to oxidation at moderate to high temperatures, but this application is not considered here since it falls within the category of composite materials.

The most notable use for molybdenum disilicide as a bulk material has been as a major constituent of resistance heating elements that can be brought to temperatures of 1650°C (3002°F) in an oxidizing environment. Other uses suggested for molybdenum disilicide shapes are in thermocouple protection tubes (for measurement of hot exhaust gases and molten bath temperatures), crucibles, and other refractory shapes (for molten materials such as glass).

Test specimens of molybdenum disilicide have been fabricated for a study of heat-resistant materials in leading edge applications. These specimens were prepared from

impure commercial molybdenum disilicide powder and were formed by slip casting and sintering.

The major obstacles to the use of molybdenum disilicide in this application were found to be the development of considerable plasticity in the specimens at 1370°C (2498°F) and above, as well as the high creep rate of the material.

Advantages and Disadvantages

As mentioned previously, the outstanding advantages of the disilicides are their oxidation resistance at high temperatures and their maintenance of high tensile strength and modulus of rupture at temperatures where most oxides and metals have low values for these properties.

The primary disadvantages of some members of this class of materials are as follows:

1. Room-temperature brittleness
2. Excessive creep at high temperatures, at least in the case of molybdenum disilicide
3. Poor oxidation resistance at low temperatures, e.g., in the 500°C (932°F) to 900°C (1652°F) range for molybdenum disilicide.

It is not known whether all of the above are intrinsic limitations of the disilicides or whether they are brought about, to some degree, by the presence of impurities in the raw materials, by lack of the desired stoichiometric ratio, or by poor fabrication methods.

Properties

Chemical Stability

There is little doubt as to the excellent high-temperature oxidation resistance of molybdenum disilicide, tungsten disilicide, and such other disilicides as have been studied. For example, slip cast and sintered molybdenum disilicide test pieces have been subjected to air flows corresponding to mass velocities of 1500 lb/ft² hr at temperatures up to 1480°C (2696°C). Very small weight changes were noted.

Studies of the mechanism of the reaction of molybdenum and tungsten disilicides in an oxidizing environment at temperatures up to 1700°C (3092°F) or higher show that the oxidation resistance of these materials results from the formation of a glassy coating of silica over the disilicide shape. These silica coatings are firmly anchored to the disilicide base and they are self-healing so that, when a break results from impact or other stress application, the coating will renew itself during continued exposure to an oxidizing atmosphere at high temperatures.

The poor oxidation resistance shown by at least some disilicides at low temperatures can be alleviated first by oxidizing the test specimen at a high temperature to insure formation of a protective silica coating which will prevent the entry of oxygen into the interior of the specimen.

Strength

Work at Brush Beryllium Company (1) on tantalum and tungsten disilicides has indicated that these materials retain high modulus of rupture values at temperatures up to

1510°C (2750°F) as shown in figure 3. Values for molybdenum disilicide reported by Bell Aircraft Corporation (2) are also given in this figure. Tungsten disilicide is particularly noteworthy as the best specimens made from it had modulus of rupture values of close to 70,000 psi at 1370°C (2498°F) and 1510°C (2750°F), a value roughly comparable on a strength-to-weight basis to values obtained on beryllides.

Thermal Properties

Various silicides have the following melting points:

<u>COMPOUND</u>	<u>MELTING POINT</u>	
TiSi ₂	1540°C	2804°F
ZrSi ₂	1520*	2768*
VSi ₂	1750	3182
NbSi ₂	1950	3542
TaSi ₂	2400	4352
CrSi ₂	1570	2858
MoSi ₂	1870	3398
WSi ₂	2150	3902

(* MELTS INCONGRUENTLY)

Recent determinations of the mean coefficients of thermal expansion of tungsten and tantalum disilicides give a value of about 4.7×10^{-6} in/in/°F between 27°C (80°F) and 2037°C (3700°F) for both compounds.

The thermal conductivities of samples of molybdenum disilicide of 95 percent theoretical density are reported as follows:

<u>TEMPERATURE</u>	<u>K</u>
° F	BTU/hr/ft ² /F/in.
70	218
390	290
1470	145

It is to be expected that other disilicides would have high thermal conductivities.

Potential Properties

One of the more serious defects of molybdenum disilicide is its high creep rate at elevated temperatures. Although creep measurements have not been made on materials of controlled purity, it seems probable that high creep is an intrinsic property of molybdenum disilicide.

In metal alloy systems it has been found that solid solutions possess more resistance to plastic deformation than does a pure metal. Increase of the concentration of the solute

decreases the rate of creep. After the limit of solid solubility of the solute has been reached, and the excess then appears as a dispersed phase, creep is further retarded because the stress required to move dislocations is increased by the presence of the dispersed phase.

To insure persistence of the dispersed phase at elevated use temperatures, it will be necessary to have that phase present in a concentration which will exceed its solid solubility at the use temperature. Therefore, it would seem advisable to concentrate efforts on a relatively few pseudo binary systems of the silicides. One that appears promising is the WSi_2 - $TaSi_2$ system, both from the standpoint of the refractory nature of the end members (m.p. WSi_2 , $2150^\circ C$ ($3902^\circ F$); m.p. $TaSi_2$, $2400^\circ C$ ($4352^\circ F$)) and the incomplete solid miscibility between them. It has been shown by previous investigators (3) that at $1300^\circ C$ ($2372^\circ F$) tantalum disilicide will take up 25 mole percent of tungsten disilicide in solid solution and that tungsten disilicide will take up about the same proportion of tantalum disilicide in solid solution. Inasmuch as the disilicides are compounds of high metallicity, it may be that the resistance to creep would be increased in these combinations as is the case in metals.

The effect of the presence of small amounts of other metalloid elements on the formation or stabilization of various crystal types and possible influence on creep and other properties deserves further investigation. Thus it is known that low concentrations of carbon, nitrogen, and oxygen can result in the persistence of certain structural types in pseudo binary or ternary systems of the silicides, over concentration and temperature ranges where such structures would otherwise be metastable.

Combinations of disilicides and diborides merit further development. The Carborundum Company has found that a combination of 90 percent zirconium diboride and 10 percent molybdenum disilicide has excellent resistance to oxidation at temperatures up to $1950^\circ C$ ($3542^\circ F$). Further study is needed on the silicon-boron system, as the compound SiB_6 is surprisingly refractory (m.p. $1950^\circ C$ ($3542^\circ F$)).

Silicides References

1. Booker, Pain, and Stonehouse, "Investigation of Intermetallic Compounds for Very High Temperature Applications," Progress Reports Nos. 2, November 15, 1959; 3, February 15, 1960; 4, April 15, 1960; 5, July 15, 1960, Brush Beryllium.
2. Dukes, Anthony, and Pearl, "Investigation of Feasibility of Utilizing Available Heat Resistance Materials for Hypersonic Leading Edge Applications," April 15, 1959, Bell Aircraft Corporation.
3. Nowotny, Kudielka, and Parthe, "The Structure of Silicides," Plansee Proceedings 1955, The Pergamon Press, London, 1956.

Oxides

Refractory oxide ceramics comprise an important class among nonmetallic refractory materials, although they are by no means among the highest melting compounds. Thorium oxide, which is on top of the list, has a melting temperature of $3200^\circ C$ ($5792^\circ F$), and aluminum oxide, the oxide which so far has found the widest application, melts at $2050^\circ C$

(3722°F). Melting temperature is rarely a limitation of high-temperature structural materials. Before melting occurs some other property usually becomes a limiting factor.

Refractory oxides are outstanding for their chemical stability over a wide range, especially under oxidizing conditions. They show up well in comparison with other classes of refractory materials; nevertheless, it should not be overlooked that their stability at high temperatures is also affected by conditions of atmosphere, pressure, and contact with other materials. Uranium dioxide, for instance, oxidizes to U_3O_8 at relatively low temperature in air, but it has good stability up to its melting point if heated under reducing conditions. Al_2O_3 may be mentioned as another example. It is stable in air up to 1950°C (3542°F) but dissociates slowly in vacuum above 1800°C (3272°F) to gaseous Al_2O and O_2 .

The military opportunities of oxides as structural parts arise from those properties which point toward applications beyond the usefulness of metals and for those applications where structural use is combined with thermal and electrical insulation requirements. For structural parts, deformation characteristics and stability under intermittent and continuous load and temperature are of special significance; for thermal insulation, thermal conductivity, and heat capacity, and for electrical insulation, changes of dielectric properties with temperature must be considered.

Properties of oxide ceramics depend not only on chemical composition, but also on micro- and macro-structure of the finished article. A wide variation of mechanical characteristics is obtained from single crystals and dense, single-phase polycrystalline solids. In the case of thermal insulation, structures of well-defined porosity are of advantage.

Properties

Investigators have confined their attention almost exclusively to determining the properties of the single oxides, Al_2O_3 , BeO, MgO, ZrO_2 and ThO_2 ; Al_2O_3 receiving the most attention. Among the mixed oxides, refractory silicates, aluminates, titanates, niobates, zirconates, and phosphates have been investigated. A wealth of up to date information on properties of refractory single and mixed oxides is available in WADC Technical Report 59-448 (January 1960); however, test results obtained from various sources are difficult to compare, as microstructure, porosity, chemical composition; and test conditions are not known. Only in rare cases is such complete information available. Nevertheless, a fairly good picture of properties of oxide ceramics emerges, as test refinements continue and as improvements in preparation of test specimens of higher density are made. A brief discussion of those properties which are most pertinent for structural applications is in order.

Fracture Strength

The fracture strength of refractory oxide ceramics compares favorably with that of refractory metals, especially if one considers strength-to-weight ratio. The effect of temperature on the strength of oxide bodies has not been studied intensively. The best data is available for sintered aluminum oxide which at the present state of the art, exhibits the highest fracture strengths among the refractory oxides. For instance, a tensile strength of 35,000 psi at room temperature has been reported. Eighty percent of the strength is retained up to 1100°C (2012°F). Around 1200°C (2192°F) a considerable drop in strength occurs and at 1370°C (2498°F), minimum limit of high temperature as defined for this report, only about 10 percent of the room temperature strength remains.

Other refractory oxides such as BeO , ThO_2 , MgO , and ZrO_2 follow a similar pattern; if their room temperature strengths can be brought up to that of Al_2O_3 , it may be expected that they will retain 10 percent of their strength at higher temperatures than Al_2O_3 .

In general, strength values have improved steadily during recent years, due to improvements in processing methods which have led to higher density, lower pore content, and better control of microstructure.

Impact resistance has also gone up, but not to the same extent that flexural strength and density have been improved. Major significant improvements in impact strength can only be expected as a result of solving the problem of brittle fracture of oxide ceramics. It is well-known that ductility at room temperature has been observed on certain oxide single crystals; there are no signs at present that room-temperature ductile polycrystalline oxide ceramics can be produced. It has been found that the impact strength of Al_2O_3 and MgO actually decreases between room temperature and up to 1600°C (2912°F), although plastic deformation is known to occur within this temperature range under slowly applied load.

Thermal Shock Resistance

Refractory oxide ceramics are known for their low thermal shock resistance in comparison with other materials. Improvements may be expected, but they will be only marginal unless an order of magnitude increase in strength is achieved. More important than improving physical properties, seems to be an improvement of the shape factor which also enters into the thermal shock equation. It points toward the usefulness of shapes of small cross-sectional area, such as fibers, platelets, etc., to reduce the thermal gradient.

Stability and Oxidation Resistance

The relatively high chemical and thermal stability and oxidation resistance of oxide ceramics make them attractive as materials of construction for high-temperature applications. Thorium oxide is the outstanding material which is stable in air up to 3200°C (5792°F). To make full use of the favorable high-temperature properties of oxides, it is important to use high purity materials. Small amounts of oxide impurities lower melting temperatures appreciably, as can be seen from phase diagram studies.

Vapor pressure data of oxides are fairly well established; work on the chemical interaction of oxides with varying types of gases at high temperature is in progress.

The interaction of oxides in contact with metals has been studied, but more information will be necessary. Little is known about diffusion mechanisms and rates of gas flow through oxide layers at high temperatures and under varying service conditions.

Dielectric Properties

These properties, not relevant for structural uses, but important as secondary considerations, should be mentioned, especially in the case of refractory oxides. BeO , MgO , and Al_2O_3 remain electrical insulators to higher temperatures more than any other dielectric with the possible exception of boron nitride.

Potential

A steady improvement of the physical properties of refractory oxides can be foreseen. As in former years, these improvements will come about by better processing methods, rather than by compositional changes. A recent significant achievement in this direction has been the production of pore-free, transparent aluminum-oxide ceramics by the General Electric Company. If oxide ceramics are to be used, then shape and design factors will take on considerably more importance. Ways must be found to use oxide ceramics in the form of small units of high strength, such as thin sheets, platelets, or fibers, either as built up units or in composites for reinforcements. Thin oxide sheets may be laminated between metallic sheets; platelets may be used in protective coatings for metallic or other substrates, and continuous fibers may be woven into textiles or ropes.

It seems doubtful that ceramic oxides, per se, in solid sections will find uses as structural materials, but they will be used for protection of other materials, as coatings, and for low stress applications where thermal or electrical properties are the prime consideration.

Oxide References

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3. OTS PB 161194 - February 26, 1960 - DMIC, Memo 44, Refractory Materials. Defense Metals Information Center, Battelle Memorial Institute, Columbus 1, Ohio.
4. Lockheed Aircraft Corporation - LMSD-2466 - January 15, 1959. "Properties of Refractory Materials," Collected data and references.

Brittle Behavior

Design Technology

Design technology for brittle materials has not been established. This puts a major limitation on the use of brittle materials in load-bearing components. Particularly in air vehicles where weight and size are critical, one does not want to use a component that can withstand safely, for example, a 1000-pound load when the maximum load is only 100 pounds. Conversely, the component must be safe.

Present knowledge of how to design structural members with brittle materials is inadequate for their use in reasonably efficient and safe designs. An allowable stress cannot be assigned logically. It follows that knowledge of how to evaluate resistance to load (strength) of brittle materials probably is inadequate.

It is known that the stress at which a given brittle material will fracture depends on size and stress-state as well as time, temperature, and atmosphere. It is known that the

reproducibility of brittle failure stress as measured in a controlled test is poor compared with the reproducibility of yield stress in ductile failures. Although progress has been made, knowledge of these effects is inadequate for the quantitative treatment needed to design safe structures. Thus, one problem area is that of establishing relationships that adequately describe the conditions under which a load will cause a brittle material to break.

The strength behavior of brittle materials is altogether different from that of ductile materials, and failure criteria developed for ductile materials cannot be used to design with brittle materials. Unlike ductile materials, where a shear component of the applied stress causes deformation failure, a tensile component of the applied stress is critical in fracturing brittle materials. Also, once started, a fracture crack can propagate rapidly without additional load applications, whereas additional stress is required to extend a plastic deformation. In this connection, relief of a stress concentration in a brittle material by fracture permanently damages the structure, while little or no damage is caused when plastic flow in a ductile material removes a concentrated stress. As another major difference, size effects need not be considered in the failure of ductile materials.

It is widely accepted that a "flaw"* initiates fracture by concentrating stress in a localized volume. The fracture propagates when the stored elastic energy exceeds the energy required to form a new surface.

As a consequence of fracture being initiated by a flaw, unlike the case of ductile materials, strength must be treated by considering brittle materials as inhomogeneous. This is done best apparently by the so-called "statistical theories" of failure. In the statistical concept, the scatter in fracture stress from nominally identical specimens tested under the same conditions becomes an intrinsic property of each material, and strength is not defined in terms simply of stress and/or strain. Further, in this concept, one can separate into two types the external factors that affect strength:

1. The "statistical" ones (i.e., those that determine the number of flaws acted on in given material) such as size, shape, stress distribution and, perhaps, stress type (combined stress).**
2. The "material" ones such as temperature and time (strain rate, creep, fatigue).

To develop a design technology, it is necessary that we learn to handle confidently the statistical effects. Several methods have been proposed to do this. The most widely known method is the one Weibull originated. More general methods have been proposed; Weibull's and other solutions based on a failure behavior analogous to that of a chain breaking at the weakest link are special cases. These may not be statistical methods most generally useful, or most applicable to the ceramics of present interest.

Adequate experimental control is extremely difficult to achieve in investigating the "statistical" effects. This probably is the major reason that a general design technology

* In addition to the normally considered types, the flaws might be crystal-lattice imperfections, frozen-in local stresses in grains, a grain boundary, etc.

** In some recent British work, these factors have been treated from the view that a brittle material is composite, consisting of a skin and core, each with its own mechanical properties. This view is felt to warrant consideration as well as the statistical approach.

for brittle materials is not at hand. Without extreme care, uncontrolled variables in specimen preparation or in strength testing are likely to influence data and, if unrecognized, to cause erroneous conclusions. Also, peculiarities of a specific experimental material can confuse interpretation of data. For example, the marked effect of moisture on the strength of glass and periclase crystals causes doubt as to their suitability as experimental materials for developing a general design technology.

Probably the greatest need in establishing a design technology is for a body of fracture-stress data obtained under conditions of extreme control, i.e., where unknown extraneous stresses in testing or uncontrolled variables in specimen preparation have not had an influence. Controlled variables in this data should include such factors as type of ceramic, size, stress state, and perhaps strain rate.

Once the design relations have been developed, the problem of developing or selecting test methods and procedures for furnishing the data necessary to use these relations requires attention. Hence, in addition to research on determining an applicable criteria for failure, research probably will be needed on testing techniques to obtain the strength data that will allow full and proper consideration of ceramics in mechanical-design work.

Effects of Microstructure

The strength of a ceramic is known to be a function of microstructural* features, and they in turn, depend on the processing methods and conditions used to prepare the ceramic. Knowledge is incomplete concerning the microstructure that would give best strength properties, and on the effects of processing variables which determine microstructure or strength properties of a ceramic. Such knowledge could lead to ceramics with improved strength properties, and lead to their greater utilization in load-bearing applications.

Any change in processing a ceramic can be expected to affect its strength properties, and the potentialities for improving ceramics through research in this area appear to be great. Theory suggests that a flaw-free ceramic should withstand stresses in the million-psi range, whereas present ceramics fail in the thousand-psi range.

Data have been obtained showing that, in general, fracture strength increases with decreasing porosity (at least so long as pores are located near grain boundaries) and is related to grain size in a ceramic body. In some brittle materials, strength is affected greatly by surface character. There are undoubtedly other features of a brittle material that can affect strength but that are not yet recognized, such as crystal structure, grain boundary conditions, trace impurities, etc.

Present knowledge of ceramic processing is inadequate to provide ceramics in which pore removal and grain growth can be extensively controlled. Ceramics are made by compacting powders and heat treating the compacts. During the heat treating, in the refractory materials of interest, the compacted powder undergoes sintering reactions. These reactions are manifested by bonding together the powder particles, a material transport that fills pores between mismatched neighboring pores and causes certain particles to grow at the expense of others. The driving force for these reactions is the free surface energy of the particles, and the most widely held theory is that densification occurs by a vacancy-diffusion mechanism in solid-state free sintering and by viscous flow in hot pressing, or if a liquid phase develops.

* Including pore structure and, perhaps, crystal structure.

To attain ultimate strength in a ceramic it becomes quite important that we understand these sintering reactions better. By this means, sound guidance can be given to the selection of processing conditions that will yield the strongest body structure. Variables in the processing that are known to influence sintering, and whose effects require further elucidation through research, include:

1. Physical form of the starting powder
2. Contaminants
3. Compacting conditions
4. Sintering atmosphere, pressure, and temperature schedule.

Other Studies

In addition to the problems of a fracture criterion for brittle materials and of improving the strength properties of ceramics, there are other problems that require research before maximum utilization can be made of ceramics in load-bearing applications.

When the temperature is raised, a point is reached with most stressed brittle materials where plastic flow occurs, and information on this transition area is important. However, it has been studied very little. A first question demanding an answer is whether a material can sustain useful loads once the transition is reached and, if so, what strength criterion can be used in mechanical design. Another area for inquiry concerns ceramic factors, i.e., study of the effects of variables in composition and body structure of the ceramic on the conditions for, and the nature of, this pyroplastic flow.

Under special conditions, plastic flow rather than fracture is observed at room temperature in certain inorganic nonmetallics, indicating that brittleness is not an inherent quality of ceramics. Therefore, research on improving the strength properties should treat not only the problem of increasing the fracture stress, but also that of lowering the yield stress. If, for example, a change in body structure decreases the brittle strength of a ceramic but increases its tendency to yield, sufficient change in this direction might provide a ductile ceramic. Experiments in this area are hampered because there is no method for measuring the tendency to yield nominally brittle materials. However, indenter- and hydrostatic-loading techniques appear to warrant investigation. Indenter methods are additionally attractive as tools for studying brittle-strength behavior, since they offer the possibility of measuring the energy required to propagate a crack and of stressing only the interior of a ceramic body in tension, as opposed to usual methods, which apply tensile stress to the surface or to both the surface and the interior.

Applications and Requirements for Ceramics and Intermetallics

The previous sections for the most part taken from Report MAB-169-M were primarily concerned with describing the present state of the art of those refractory inorganic nonmetallics that have or promise a potential as high temperature structural materials. The applications where the refractory inorganic nonmetallics have potential include such items as: wing and body panels for thermal protection, leading edges of glide re-entry vehicles, re-entry nose cones, rods for nuclear fuel elements, high temperature seals and bearing, insulative structures for hot areas of propulsion systems (ramjets and solid propellant rockets), coatings and diffusion barriers for refractory metal protection, and

electrical insulation for communication and navigation equipment. Although these items are representative, they are, however, only a fraction of the many possible applications for these materials.

It must be realized that the step from potential to actual use is a great one, one that will only come about through intensive well-planned research efforts directed to the anticipated problems associated with the advanced and future aerospace systems. What then are a few of these anticipated problems and what will be required of the structural materials in the near future?

The environmental conditions of advanced propulsion and atmospheric re-entry aerospace systems will provide an indication of the enormous magnitude of these problems and future material requirements. Of greatest concern are the induced environments, those which will be generated by the advanced systems during their flight path or operational period. The environments chosen for consideration include those of the glide re-entry vehicle, ballistic re-entry body, and solid propellant rocket motor.

Glide Re-entry Vehicle

The induced environment imposed by the specific configurations or design parameters of a glide re-entry vehicle varies in accordance with the position of the vehicle along its three phase flight trajectory, i.e., boost, orbit, and re-entry. The environment consists of various factors such as: accelerations and decelerations, noise, wind loads, shock, vibration, moderate to large dynamic pressures, large total integrated heat fluxes, and very high temperatures. The re-entry phase of the flight trajectory produces the severest conditions as temperatures, heat fluxes, and decelerations are at their maximums. It is these three factors that are responsible for the most significant materials problems. Although it is possible to vary the magnitude of these factors through variations of the flight trajectory, the following typical values are an indication of the severity of the induced environment for various families of glide vehicles. Decelerations may vary between 1 and 50 G's and the hot areas of the vehicles will experience heat fluxes between 50 and 300 BTU/ft²/sec with total heat inputs varying between 10,000 and 400,000 BTU/ft² and maximum temperatures between 2500°F-8000°F (1371°C-4426°C) with associated exposure times of 20 to 60 minutes. The re-entry velocities of the gliders will vary with their mission. Re-entry velocity is approximately 26,000 feet per second from an Earth orbit and 36,000 feet per second from a Lunar mission.

Ballistic Re-entry Body

The ballistic re-entry body under consideration here is the nose cone of the weapon delivery section of an intercontinental ballistic weapon system.

Except for severity, the type of induced environment for a ballistic re-entry body will be similar to that of a glide vehicle. The temperatures and heat fluxes for nose cones will be of significantly higher magnitude with the following typical values; stagnation temperatures of 3800°F-15,000°F (2093-8316°C), on an advanced ablation body stagnation temperatures will probably not exceed 5000°F-6000°F (2760-3316°C). Heat fluxes will vary between 200-4000 BTU/ft²/sec, however, exposure times are much shorter than for a glide vehicle (<1 min). In addition, total heat inputs are less, perhaps one half order of magnitude for the most advanced designs.

Solid Propellant Rocket Motors

Of the material considerations for future solid propellant rocket motors, those of the nozzle are the most challenging and are a direct result of the recent advances in obtaining higher performance propellants to propel the heavier payloads of the advanced systems. The two service environmental parameters generated by these advanced propellants that are responsible for the materials problems are: flame temperatures of 5000°F-8000°F (2760°C-4426°C), and an exhaust gas that is extremely reactive. In addition, the firing durations of the advanced solid propellant rocket motors may extend up to 2 minutes, nearly twice those of present generation motors; because of the metallic additives there may be, depending upon the magnitude of the flame temperatures, an increase in the amount of particulate matter in the exhaust gases, also, associated exhaust velocities may vary from 5000 to over 8000 feet per second.

Design Philosophies

For the re-entry applications (i.e., leading edges, nose cones, wing and body panels), various materials approaches have been suggested and each approach will depend upon the design philosophy chosen to accomplish a given mission, (i.e., ablative, radiative, heat sink, or cooled structure). The refractory inorganic nonmetallics have been suggested as candidate materials for incorporation into most of these thermal protection mechanisms.

The solution of the solid propellant rocket nozzle materials problem will lie in the development of nozzle materials systems. The rocket nozzle materials system has been described as, "a complex of materials, each selected for a particular primary function within the system and each of which, in turn, modifies the environment to which the associated materials are subjected".* This approach has developed since there is no ideal nozzle material and it is synonymous, in principle, to the thermal protection systems of re-entry vehicles.

Basically, the nozzle materials systems will consist of the following elements: a flame barrier (erosion resistant) layer which is exposed to the direct impingement of the exhaust gases; a load bearing member, or shell which is designed to carry the structural or dynamic loads, and an intermediate layer or temperature moderator which could consist of an insulator, conductor, or heat sink material or a combination of the three, so placed as to reduce the heat transfer to the load bearing member.

Although the results of simulated and actual rocket firings that were concerned with describing the potential of ceramics as nozzle inserts were not encouraging, ceramics are one of the classes of candidate materials being considered for use in nozzle materials systems. Their potential, in the main, is the interesting insulative characteristics possessed by certain ceramics, notably the oxides. While other ceramics possess interesting properties, i.e., extremely high melting points, high temperature stability, etc., information is not available which adequately describes their ultimate potential as components of nozzle materials systems.

Research Aims

The potential applicability of the refractory inorganic nonmetallics to the aforementioned re-entry and propulsion protection mechanisms, as well as to other applications, has been indicated in many instances through cursory investigations on materials frequently poorly

* Report MAB-158-M, Vol II, 30 Nov 1959

characterized in terms of impurities, microstructure, process controls, bonding, etc. Through research directed towards obtaining well-characterized materials, along with the substantial property improvements that are expected to result, it will undoubtedly be demonstrated that these materials, by virtue of their other characteristics, possess an increased capability for structural and propulsion applications.

However, whatever the degree of optimism that may prevail by the nature of the improvements resulting through research, the refractory inorganic nonmetallics (ceramics) will probably remain brittle materials. One must therefore obtain a fundamental understanding of the nature of brittle fracture. In addition, it is mandatory that the eventual utilization of ceramics as load bearing members must rely on the establishment of a design technology for brittle materials. The structural designer must possess information that will enable him to incorporate brittle materials in his designs. Although present knowledge is lacking on how to design with brittle materials, it has been proven that if proper consideration is given to brittle material characteristics, through proper design philosophies, reliable structural components are obtained.

It should be quite evident that much remains to be accomplished towards achieving the degree of technology that will permit the utilization of those ceramics and intermetallics that have structural potential, thereby, hastening the solution of many of the materials problems associated with our advanced and future aerospace systems.

Applications and Requirements References

1. WADD Technical Report 60-716, Part I, (U) Materials Requirements for Advanced and Future Air Force Weapon Systems, dated October 1960.
2. Report MAB-151-M, (U) Report on Thermal Protection Systems, dated June 1959.
3. Report MAB-158-M, Standing Review of Department of Defense Materials Research and Development Program, Vol II, dated November 1959.
4. Report MAB-169-M, Report of the Ad Hoc Committee on Refractory Inorganic Non-metallic Structural Materials, dated January 1961.

TABLE I

<u>COMPOUND</u>	<u>MELTING POINT</u>
TiB ₂	> 2600 C (4712F)
ZrB ₂	3000C (5432F)
NbB ₂	> 3000C (5432F)
TaB and TaB ₂	> 3000 C (5432F)
HfB ₂	3060 C (5540F)
ThB ₂	> 2500 C (4532F)
90% ZrB ₂ , 10% MoSi ₂	> 2360 C (4280F)

TABLE 2
SUMMARY OF INTERMETALLIC COMPOUND PROPERTIES
(as currently available)

	ZrBe ₁₃	NbBe ₁₂	TaBe ₁₂	MoBe ₁₂	Ta ₂ Be ₁₇	Hf ₂ Be ₂₁	MoSi ₂	TaSi ₂	WSi ₂
MELTING POINT, °F	3500	3070	3360	3000	3610	>3500	3690	4350	3960
X-RAY DENSITY, g/cc	2.72	2.91	4.18	3.03	5.05	4.26	6.24	9.10	9.87
MAX. TEMP. FOR 10-HOUR SERVICE IN DRY AIR, °F	3000	2900	3000	2900	3000	3000	>3000	>3000	>3200
MODULUS OF RUPTURE, 10 ³ psi									
	36	39	56	42	67	20	26	29	57
	2300°F								
	36	39	43	30	54	24	28	13	70
	2500°F								
	25	18	26	13	30	17	13	16	51
	2750°F								
YOUNG'S MODULUS, 10 ⁶ psi									
	25	25	24	15	15	28	40	50	50
	2300°F								
	20	15	14	12	11	15	25	35	48
	2500°F								
	10	10	10	1	10	10	12	14	15
	2750°F								
THERMAL CONDUCTIVITY BTU hr ⁻¹ ft ⁻² °F									
	21.0	17.9	11.0	18.2	—	—	16.4	—	—
	1600°F								
	20.8	19.0	10.5	17.5	—	—	—	—	—
	2600°F								
SPECIFIC HEAT, BTU/lb °F									
	0.41	0.40	0.28	0.41	—	—	—	—	—
	1600°F								
	0.46	0.43	0.30	0.45	—	—	—	—	—
	2600°F								
THERMAL EXPANSION, 70 - 2600 °F 10 ⁻⁶ in./in. °F									
	9.8	9.2	8.3	—	8.57	9.05	4.80	4.67	4.4

TABLE 3
OXIDATION DATA FOR SELECTED INTERMETALLIC COMPOUNDS

COMPOUND	PERCENT OF ABSOLUTE DENSITY	TEST TEMPERATURE °F	WEIGHT GAIN (mg/cm ²)				MILS - PENETRATION	
			1 HOUR	5 HOURS	10 HOURS	MEASURED	CALCULATED	
TaBe ₁₂	98.9	2900	1.9	3.9	5.9	0.2	0.7	
TaBe ₁₂	97.8	3000	11.3	25.4	36.6	3.1	4.3	
Ta ₂ Be ₁₇	98.8	2900	2.6	8.4	16.5	0.7	1.9	
Ta ₂ Be ₁₇	99.6	3000	7.9	15.2	33.0	1.9	3.8	
Hf ₂ Be ₂₁	94.7	2900	1.5	3.7	4.8	<1.4	0.6	
Hf ₂ Be ₂₁	100.	3000	13.1	32.5	59.1	—	7.6	
Hf ₂ Be ₁₇	88.2	2900	7.8	10.2	14.3	<2.8	1.8	
Hf ₂ Be ₁₇	88.5	3000	9.7	21.2	31.9	5.2	4.1	
TaSi ₂	96.3	2900	0.8	1.4	1.4	<0.7	0.1	
TaSi ₂	99.8	3000	0.9	1.6	2.4	0.1	0.3	
WSi ₂	98.7	2900	(-0.5)	(-0.4)	(-0.3)	<0.8	—	
WSi ₂	98.8	3000	0.2	1.7	1.9	0.5	0.2	
MoSi ₂	94.9	2900	0.7	0.8	1.0	0.3	0.1	

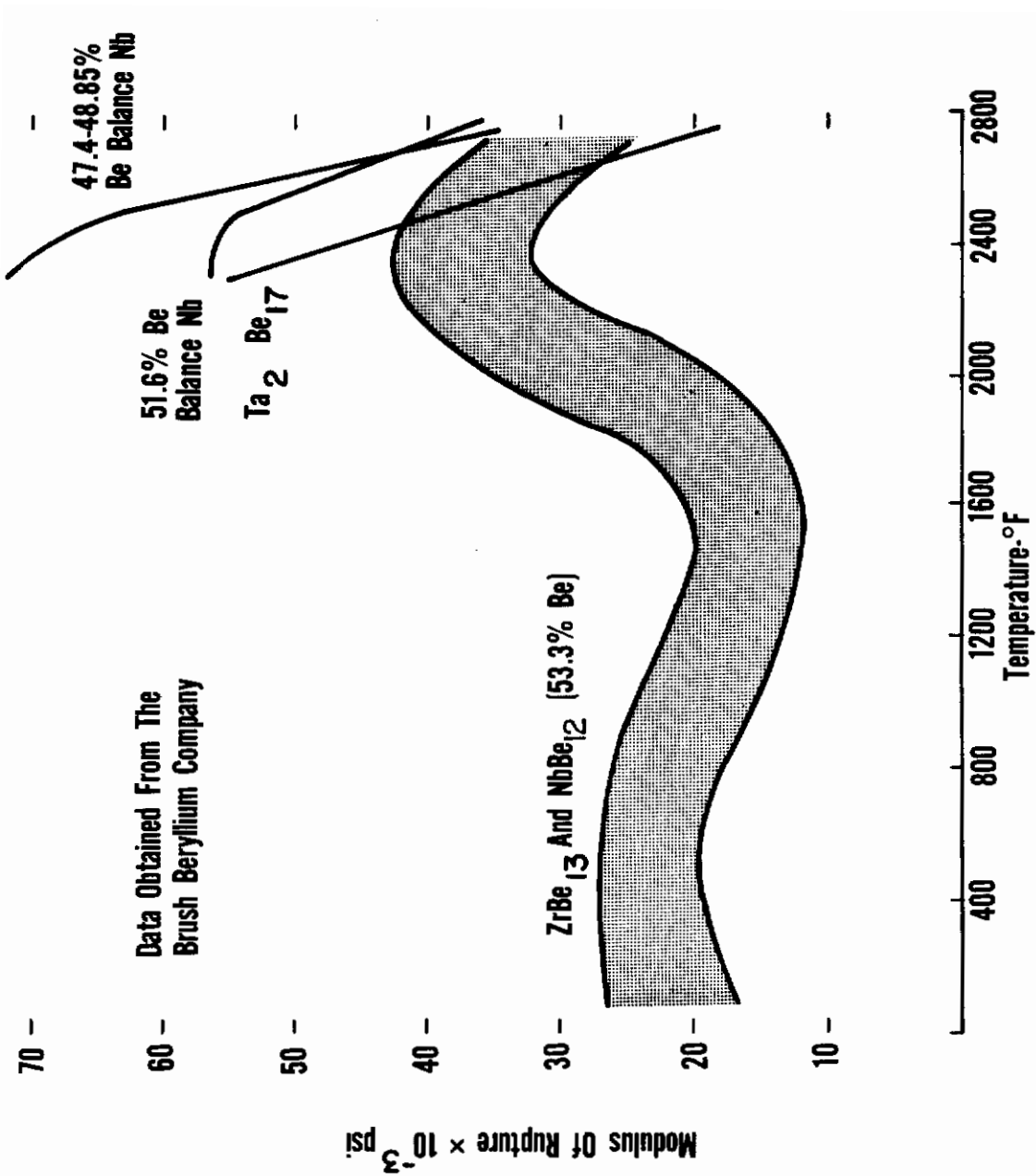


Figure 1. Mechanical Property Trends

(From Data Of Booker, Stonehouse & Paine, Brush Beryllium Co., 1960; And
 Additional Data Of Dukes, Anthony & Pearl, Bell Aircraft Corp., On Mo Si₂, 1959)

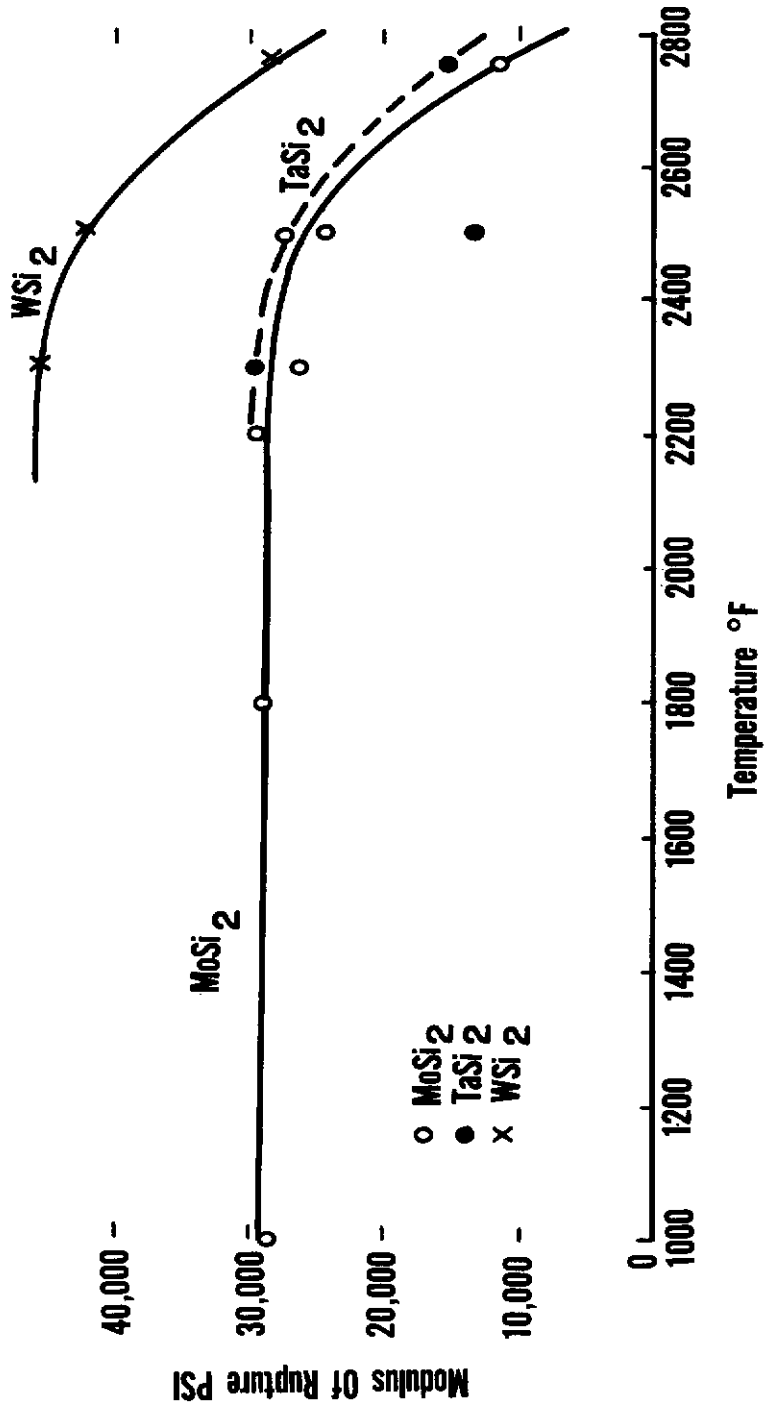


Figure 2. Oxidation Test Data

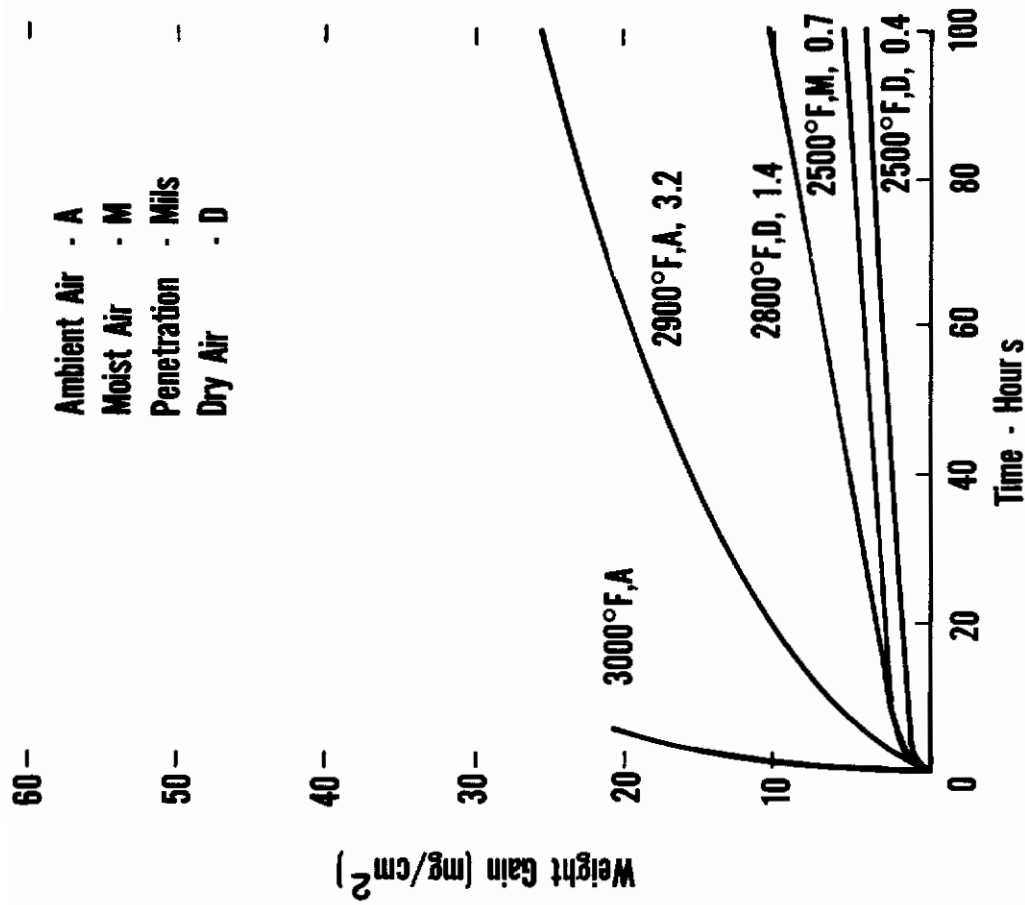


Figure 3. Modulus of Rupture vs. Temperature for Silicides